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Elasticity of hcp cobalt at high pressure and temperature: a quasi-harmonic case

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We performed high-resolution inelastic x-ray scattering measurements on a single crystal of hcp cobalt at simultaneous high pressure and high temperature, deriving 4 of the 5 independent elements of the elastic tensor. Our experiments indicate that the elasticity of hcp-Co is well described within the frame of a quasi-harmonic approximation and that anharmonic high-temperature effects on the elastic moduli, sound velocities and elastic anisotropy are minimal at constant density. These results support the validity of the Birch's law and represent an important benchmark for *ab initio* thermal lattice dynamics and molecular-dynamics simulations.

The elastic properties of hexagonal-closed-packed (hcp) metals at high pressure and temperature have attracted significant interest as benchmarks for the validation of first principle calculations as well as for their important role in geophysical processes [1–17].

Commonly, first principle methods based on density functional theory are used to calculate physical properties of materials over a wide range of P-T conditions. While in principle these calculations can provide accurate estimates for several properties, including the stable crystal structure and phonon spectra, in many cases different theoretical approaches lead to quite conflicting results. This is especially true for thermal calculations [3–9]. Specifically, a first-principle study of the elasticity of hot-dense hcp-Fe [6] suggests that at high temperature, the single-crystal longitudinal anisotropy has the opposite sense with respect to that at low temperature [1, 2]. Such conclusions are of critical importance when attempting to model the observed seismic anisotropy of the Earth's inner core. However, this change in the form of the anisotropy is not reproduced in other theoretical works [7–9].

While particularly relevant to Earth Sciences, this is but one example of diverging theoretical predictions that beg for direct experimental validation. Unfortunately, experiments probing phonon properties, in particular those of opaque metallic samples, are at the cutting edge of modern techniques. These experiments are very challenging even if involving the only high pressure [10–13, 15] and presently very few results exist at simultaneous high pressure and temperature [14, 17]. Recently, the Debye velocity, and by inference, the shear-wave sound velocity (V_S) and the compressional-wave sound velocity (V_P), of hcp iron have been determined by nuclear resonant inelastic x-ray scattering (NRIXS) in a laser-heated diamond anvil cell (DAC) [14]. This study shows a negative correlation between sound velocities and temperature at constant density and suggests an anharmonic behavior of hot, dense iron. These results are very interesting not only for their intrinsic value, but also because they cast doubt on the validity of the so-called Birch's law [18], which suggests that V_P should scale linearly with density or, in more general terms, that the elastic properties of compressed materials are well described within the framework of a quasi-harmonic approximation. In contrast, high-pressure and high-temperature sound velocity measurements on an iron-nickel alloy [17], as well as *ab initio* finite temperature molecular dynamics simulations on hcp-Fe, bcc-Fe, FeS, FeSi and magnesium silicate perovskite [9, 19] indicate that the compressional and bulk velocities at constant density are temperature independent. Possible explanations for such disagreement are the difficulty in performing calculations at simultaneous high pressure and temperature, and the complex data treatment necessary for the analysis of NRIXS spectra obtained from a sample compressed in a laser heated DAC, without an *in situ* determination of density. In particular, the use of a harmonic model in the data reduction [14] to ultimately argue for an anharmonic behavior is at some level odd. More importantly, the reliance on high-temperature parameters from a thermal equation of state (EOS) [20–22], to both solve for V_P and V_S from the Debye velocity and to obtain the hcp-Fe density, introduces large external uncertainties. This is especially true for iron, where various studies of the high-temperature EOS give quite different results [6–9, 20–26].

Thus, given the importance of hcp metals in general, and the conflicting experimental and theoretical results, we have performed inelastic x-ray scattering (IXS) measurements on single crystals of hcp cobalt hydrostatically compressed in a resistive-heated DAC. IXS is particularly well suited for studying elasticity at high pressure and temperature. However, given the relatively long counting times necessary for accurate measurements (typical integration time for single crystals are of the order of 60 s per energy point), the experiments require a high degree of time stability and reduced temperature gradients. Thus, while laser heating is at the limit of feasibility, we have opted for a locally resistively heated DAC. Our choice of hcp cobalt as the focus of this study is motivated by

the fact that it provides a suitable physical analogue for the elastic properties of hcp iron [2, 13, 16, 27], with the advantage that, unlike iron, hcp cobalt can be studied as a single crystal over a wide thermodynamic range [28]. Furthermore, the elastic tensor of hcp cobalt at high pressure and ambient temperature is well known, and experimental results [13, 15] and athermal calculations [2] are in good agreement.

We carried out our experiments on the ID28 beamline at the European Synchrotron Radiation Facility in Grenoble, France. The instrument was operated using the Si (9 9 9) configuration, which provides a total instrumental energy resolution of 3 meV full-width-half-maximum (FWHM), and a momentum resolution of 0.3 nm^{-1}. The transverse dimensions of the focused x-ray beam were $25 \times 60\ \mu m^2$ (horizontal $\times$ vertical, FWHM), further reduced by slits when necessary. Other experimental details can be found elsewhere [12, 13]. The single crystals (40 μm diameter, $\sim$ 20 μm thick, with surface normal parallel to the [110] direction) were prepared according the procedure described in [29], and loaded in a DAC equipped with 350 μm culet diamonds, using rhenium gasket and neon as pressure transmitting medium. Typical mosaic spreads (rocking curves) amounted to 0.2 to 0.3 degrees, and no degradation was observed with pressure or temperature.

Using an analogue approach to that used in previous high-pressure and ambient-temperature velocity and density measurements [13], we determined select elements of the elastic tensor at simultaneous high pressure and temperature, namely the elastic moduli C_{11}, C_{33}, C_{66} and C_{44}. We used a new DAC design specifically optimized for IXS experiments on single crystals, in order to collect high quality data on phonons at high pressure in the 300-1000 K temperature range. Examples of the collected spectra are reported in Fig. 1. While the cells have proved capable of higher temperatures, we limited our investigation to below 1000 K in order to minimize any potential anomalous effects due to the proximity of the Co hcp-to-fcc phase transition [28]. The pressure was determined in situ by the shift of the fluorescence line of a $SrB_4O_7 : Sm^{2+}$ chip placed in the sample chamber [30], while the temperature was determined from two thermocouples placed in contact with each diamond and crosschecked with the Stokes/anti-Stokes ratio of the collected phonons. Most importantly, all our measurements have been performed at constant density, determined directly from diffraction patterns collected in parallel to the IXS measurements. We directly obtained the sound velocities from the initial slope of selected acoustic modes and derived the elastic moduli by solving the Christoffel equations [13]. Typical errors are $\sim$ 2% for the sound velocities and 3-4% for the elastic moduli.

The evolution of the measured C_{ij} with temperature at constant density is illustrated in Fig. 2. At a density value of $9.40 \pm 0.02\ g/cm^3$, corresponding to a compression ratio $V/V_0 \simeq 0.947$, we observed no measurable temperature effects. This suggests that the elasticity of hcp cobalt is well described within the frame of a quasi-harmonic approximation, where the elastic properties are, irrespective of the specific pressure-temperature conditions, functions of only density. Accordingly [36],

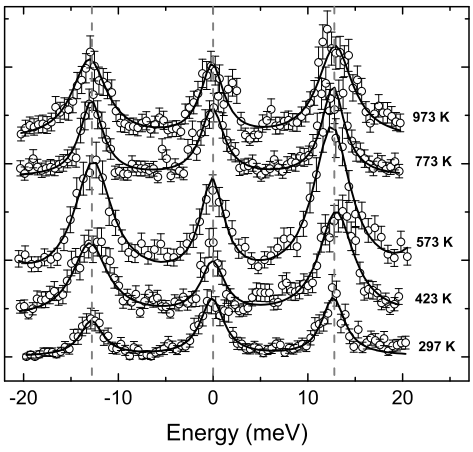

FIG. 1: Representative IXS spectra of single crystal hcp Co at high pressure and high temperature (experimental data and fits). The spectra have been collected at constant density ($\rho = 9.40\ g/cm^3 \leftrightarrow V/V_0 \simeq 0.947$) and at the reported temperatures. The vertical lines are guide to the eyes fixed at 0 energy (quasi-elastic line) and at the energies of the Stokes and anti-Stokes LA[1.1,0,0] phonons at ambient temperature.

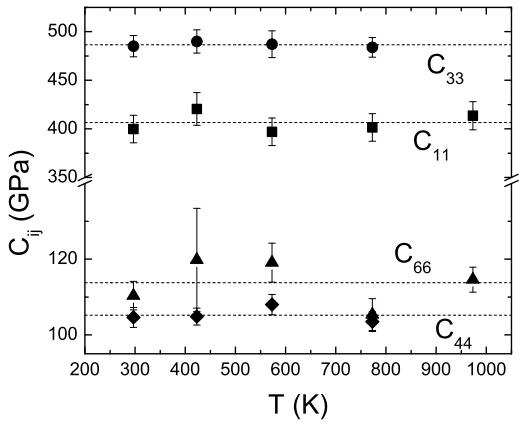

FIG. 2: Temperature evolution at constant density ($\rho = 9.40\ g/cm^3 \leftrightarrow V/V_0 \simeq 0.947$) of selected elastic moduli of hcp cobalt. The lines through the experimental points are guides to the eyes fixed to the mean values of the moduli over the investigated temperature range.

we argue that the shape of the elastic anisotropy determined at high pressure and ambient temperature [13] remains the same over a wide P-T range (at constant density). In support of the robustness of these conclusions, we note that our measurements have been performed at moderate compression ($V/V_0 \simeq 0.947$), where any anharmonic effect should be more evident [37].

These results on hcp cobalt are in apparent disagreement with the *ab initio* calculations on hcp iron, which suggests a profound change in the sense of the longitudinal anisotropy at high temperature [6]. Indeed, in the latter study, at constant density, the axial ratio c/a increases significantly with increasing temperature, ultimately leading to the crossing between C_{11} and C_{33} and to the reversal of the elastic anisotropy. As pointed out in other studies [7–9], this discrepancy between our experiments and the computations [6] might arise from the approximations used in the calculations, or be simply due to the lower temperatures we probed (possibly in a regime where these anharmonic effects are not present). Alternatively, there may be significant differences in the behavior of hcp cobalt and hcp iron at high temperature, with Co having a more harmonic inter-atomic potential. NRIXS experiments on polycrystalline hcp-Fe compressed in a laser-heated DAC have been interpreted to indicate significant anharmonic effects at moderate pressures [14]. However, the authors also suggest that temperature effects, especially on V_P, are suppressed at megabar pressure as a direct consequence of the reduced thermal expansion of highly compressed iron [20, 22–26]. The analysis of the NRIXS data uses an isobaric thermal expansion coefficient $\alpha = 5.7\times10^{-5}K^{-1}$ and a Grüneisen parameter $\gamma = 1.78$ [20, 21], while thermal calculations using $\alpha = 1 \times 10^{-5}K^{-1}$ and $\gamma = 1.5$ generate velocity-density relations in agreement with the Birch law [9]. In the case of hcp cobalt ($\alpha = 3.65-4.1\times10^{-5}K^{-1}$, $\gamma = 2.1$ [31, 32]), we do not observe any high-temperature anharmonic effect in the elastic moduli, which also implies no effects on the aggregate velocities. Such a critical sensitivity to the thermal expansion coefficient and Grüneisen γ is not surprising, as these parameters are a direct consequence of the anharmonicity of the inter-atomic potential [38] Therefore, the quantity $\alpha \times \gamma$ can be qualitative seen as quantification of the anharmonic contributions to the inter-atomic potential. Fig. 3 shows this "anharmonic factor" as a function of the compression ratio for hcp-Co and hcp-Fe. While a critical discussion of the literature for the thermal expansion and Grüneisen parameter of hcp-Fe is beyond the point of this paper, it is important to observe that with the exception of [22] and [25] (different analysis of the same experimental data set), all the other studies suggest $\alpha \times \gamma$ being bigger for hcp-Co than for hcp-Fe. This qualitative comparison argues against the possibility of a significantly more harmonic potential in the case of hcp-Co with respect to hcp-Fe, and does not explain the different high-temperature behavior reported by the present IXS measurements on Co and by the NRIXS experiment on Fe. In any case, it is worthwhile re-emphasize that, in contrast to the NRIXS technique, the interpretation of IXS results, as well as our specific conclusions in regards to cobalt, do not depend on any assumptions of the thermal parameters or P-V-T EOS.

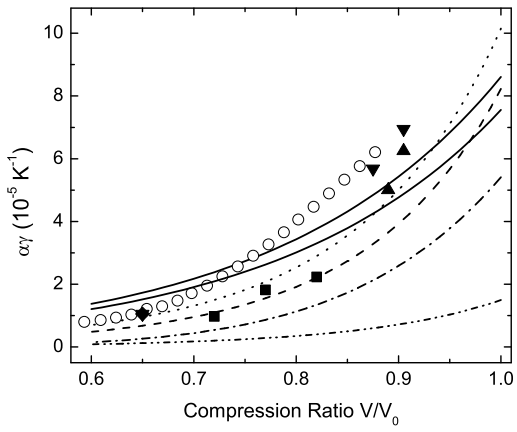

FIG. 3: Anharmonic factor $\alpha \times \gamma$ as a function of the compression ratio $x = V/V_0 = \rho_0/\rho$ for hcp-Co (solid lines [31, 32]) and hcp-Fe (open circle [25], upsidedown triangles [22], triangles [24], dotted line [20, 21], diamond [23], squares [33], dashed line [34], dash-dotted line [26], dash-dot-dotted line [9]). When high-compression data were not available, low pressure results have been extrapolated (lines in the figure) according the relations $\gamma = \gamma_0 x^q$ and $\alpha = \alpha_0 \exp\left[-\frac{\delta}{\kappa}\left(1-x^k\right)\right]$ [34], where q is a positive number ~ 1, δ is the Anderson-Grüneisen parameter and κ a positive number ~ 1.4. When numbers were not specifically provided in the individual studies, we used $q = 1$, $\kappa = 1.4$ and $\delta = 3.63$ for cobalt and $q = 1$, $\kappa = 1.5$ and $\delta = 6.5$ for iron. Extrapolations with $0.6 \leq q \leq 1.4$ or $\alpha = \alpha_0 x^\delta$, with $\delta = const$ provide comparable results, and do not change our qualitative conclusions.

In conclusion, we performed IXS measurements on hcp cobalt single crystals at simultaneous high pressure and temperature, obtaining 4 of the 5 independent element of the elastic tensor. We did not observe any quantifiable (at the 2% level) temperature effect on the elastic moduli at constant density over the temperature range 300-1000 K. Our experiments indicate that the elasticity of hcp-Co is well described within the frame of a quasi-harmonic approximation and that anharmonic high-temperature effects on the elastic moduli, sound velocities and elastic anisotropy are minimal at constant density. The quasi-harmonic behavior, shown here experimentally for hcp-Co single crystal, reported also for iron-nickel polycrystalline sample [17], and suggested by calculations in the cases of hcp-Fe, bcc-Fe, FeS, FeSi and magnesium sili-

cate perovskite [9, 19], is commonly expected for simple structures, from both the theoretical as well as empirical point of views [18]. Accordingly, in the absence of simultaneous high-pressure and high-temperature data, a functional form where velocity scales linearly with density is the most suitable representation for extrapolations to very high densities.

Finally, if we assume that the elastic properties of hcp cobalt can be used as reasonable proxy for the elastic properties of hcp iron at high pressure and temperature [2, 13, 16, 27], our results support thermal calculations [9] suggesting a quasi-harmonic behavior of iron, in apparent contradiction with the NRIXS results [14]. Especially important to the resolution of this discrepancy is an accurate measurement of the thermal EOS parameters α and γ at high pressure, as well as further experimental and theoretical work on iron to confirm the NRIXS conclusions. At present however, our experiments suggest that *ab initio* finite-temperature molecular dynamics simulations [3, 9] provide a better description of the high-pressure and high-temperature elastic properties of cobalt and iron than methods based on the particle-in-cell mode [6]. Importantly, experimental determination of phonon dispersion curves likely grants one of the most critical benchmarks for theoretical calculations [35] and, with the present work, we have demonstrated the feasibility of IXS measurements on single crystals at high pressure and temperatures, opening the door to the experimental investigation of the lattice dynamics of materials under extreme thermodynamic conditions.

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[36] We measured only 4 of the 5 independent element of the elastic tensor, missing C_{13}. However, the contribution of C_{13} to the shape of the longitudinal anisotropy is minimal.
[37] Thermal expansion of hcp-Co significantly decreases with pressure, see Fig. 3
[38] In a rigorously harmonic crystal the equilibrium size

would not depend on temperature ($\alpha = 0$), and the phonon energies, and hence the elastic moduli, would not change with the equilibrium volume ($\gamma = 0$). To account for a sizable thermal expansion and/or volume dependence of the elastic properties, anharmonic terms in the inter-atomic potential are required.